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Radionuclides in surface waters around the damaged Fukushima Daiichi NPP one month after the accident : Evidence of significant tritium release into the environment

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2019-11-01

Querfeld , R , Pasi , A-E , Shozugawa , K , Vockenhuber , C , Synal , H-A , Steier , P & Steinhauser , G 2019 , ' Radionuclides in surface waters around the damaged Fukushima Daiichi NPP one month after the accident : Evidence of significant tritium release into the environment ' , The Science of the Total Environment , vol. 689 , pp. 451-456 . https://doi.org/10.1016/j.scitotenv.201

http://hdl.handle.net/10138/331749
https://doi.org/10.1016/j.scitotenv.2019.06.362

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PII: S0048-9697(19)32935-3
DOI: https://doi.org/10.1016/j.scitotenv.2019.06.362
Reference: STOTEN 33016

To appear in: *Science of the Total Environment*

Received date: 10 April 2019
Revised date: 20 June 2019
Accepted date: 22 June 2019

Please cite this article as: R. Querfeld, A.-E. Pasi, K. Shozugawa, et al., Radionuclides in surface waters around the damaged Fukushima Daiichi NPP one month after the accident: Evidence of significant tritium release into the environment, Science of the Total Environment, https://doi.org/10.1016/j.scitotenv.2019.06.362

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Short Communication

Radionuclides in surface waters around the damaged Fukushima Daiichi NPP one month after the accident: Evidence of significant tritium release into the environment

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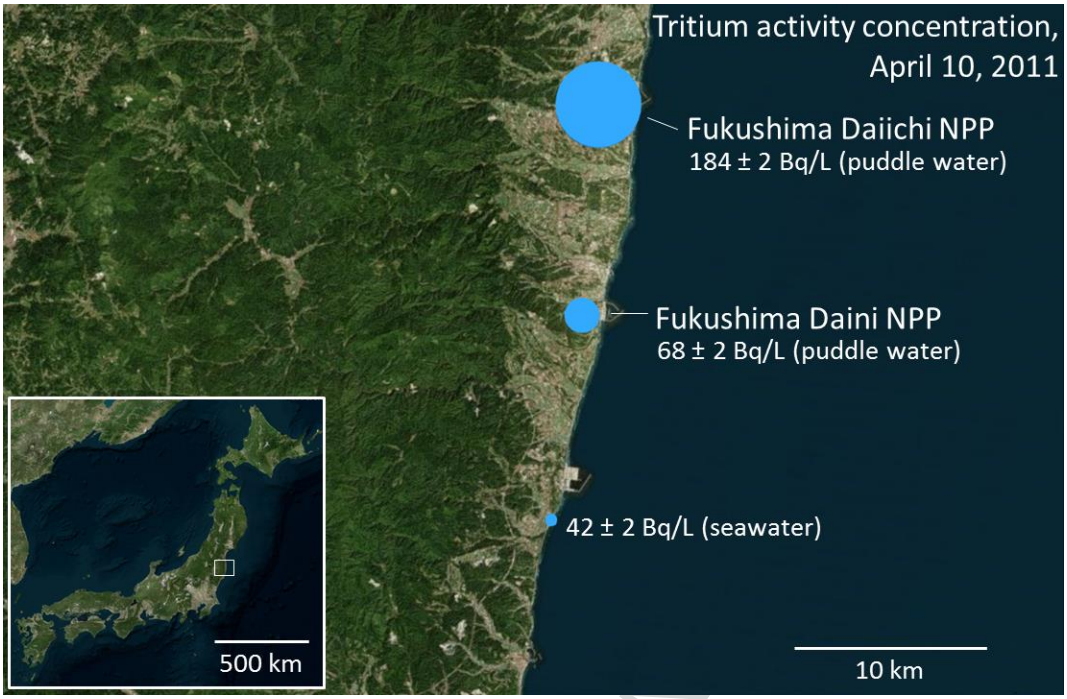
GRAPHICAL ABSTRACT



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ABSTRACT

Following the Fukushima nuclear accident (2011), radionuclides mostly of volatile elements (e.g., ^{131}I, $^{134,137}Cs$, ^{132}Te) have been investigated frequently for their presence in the atmosphere, pedosphere, biosphere, and the Pacific Ocean. Smaller releases of radionuclides with intermediate volatility, (e.g., ^{90}Sr), have been reported for soil. However, few reports have been published which targeted the contamination of surface (fresh) waters in Japan soon after the accident. In the present study, 10 surface water samples (collected on April 10, 2011) have been screened for their radionuclide content (^{3}H, ^{90}Sr, ^{129}I, ^{134}Cs, and ^{137}Cs), revealing partly unusually high contamination levels. Especially high tritium levels (184 ± 2 $Bq \cdot L^{-1}$; the highest levels ever reported in scientific literature after Fukushima) were found in a puddle water sample from close to the Fukushima Daiichi nuclear power plant. The ratios between paddy/puddle water from one location only a few meters apart vary around 1% for ^{134}Cs, 12% for ^{129}I (^{131}I), and around 40% for both ^{3}H and ^{90}Sr. This illustrates the adsorption of radiocesium on natural minerals and radioiodine on organic substances (in the rice paddy), whereas the concentration differences of ^{3}H and ^{90}Sr between the two waters are mainly dilution driven.

KEYWORDS: Fukushima nuclear accident; surface water; radiocesium; radiostrontium; radioiodine; ^{3}H

1. INTRODUCTION

In the course of the Fukushima nuclear accident (March 11, 2011), large amounts of (primarily volatile) radionuclides have been released into the environment from the damaged Fukushima Daiichi Nuclear Power Plant (FDNPP) and caused radioactive contamination of

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the Japanese mainland and the Pacific Ocean (Buesseler et al., 2011; Buesseler et al., 2012; Kinoshita et al., 2011; Povinec et al., 2013; Sanial et al., 2017; Yasunari et al., 2011). Releases (of approximately 520 PBq) (Steinhauser et al., 2014) included most notably the radionuclides of iodine, cesium, tellurium, and noble gases. Other radionuclides were emitted in smaller quantities or are difficult to detect (or to distinguish from an already existing background) and thus have been often neglected in environmental monitoring for radionuclides (Steinhauser, 2014). One of these radionuclides is tritium (^{3}H; half-life $T_{1/2}$ = 12.3 y), a soft beta emitter with a maximum energy of 18.6 keV. Tritium is produced both by (ternary) nuclear fission (cumulative thermal fission yield of about 10^{-5}) inside the nuclear fuel, as well as by neutron capture in ^{2}H or a variety of neutron-induced nuclear reactions with other nuclides such as a ^{6}Li, ^{7}Li, ^{10}B, and ^{11}B (Neeb, 1997).

However, given the fact that ^{3}H cannot be removed from water by "conventional" chemical means (Shozugawa et al., 2016), the enormous onset of ^{3}H-contaminated water on the FDNPP site will become relevant, once the storage capacities are exhausted and/or a release of the tritium-contaminated water into the Pacific Ocean will be considered by Japanese authorities (Normile, 2014). Back in 2014, a representative of Tokyo Electric Power Company claimed that tritium-contaminated water was "the most urgent matter that we have to address" (Normile, 2014). The situation remains unchanged as a recent report from the International Atomic Energy Agency (IAEA) urged the Government of Japan to "urgently decide" on a disposition path for tritium-containing water, as the planned tank capacity of 1.37 million m^3 will be reached within the upcoming 3-4 years (IAEA, 2018). Various attempts have been proposed for the removal of tritium from water, including water distillation, cryogenic distillation, vapor phase catalytic exchange, liquid phase catalytic exchange, electrolysis, combined electrolysis catalytic exchange, and a bithermal hydrogen water process (Ishizawa, 2018), however, we are not yet aware of any large-scale implementations of any of these processes on the FDNPP site. Unless a technologically feasible method for the concentration

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of tritium becomes available, the release of tritium contaminated water into the Pacific Ocean remains a realistic option to evade the storage problem. Fundamental knowledge on the existing degree of contamination with tritium, therefore, will become essential for the preparation with any upcoming battle with the "tritium trouble."

Environmental presence of tritium is often quantified in "tritium units" (TU), which is defined as 1 tritium atom per 10^{18} hydrogen atoms ($^{3}H/^{1}H = 10^{-18}$) or an ^{3}H activity concentration of 0.118 $Bq \cdot L^{-1}$. Reports on tritium in the environment after the Fukushima accident are relatively scarce (Kaizer et al., 2018; Kakiuchi et al., 2012; Kanda et al., 2015; Kashiwaya et al., 2017; Kumamoto et al., 2015; Maruoka et al., 2017; Matsumoto et al., 2013; Povinec et al., 2013; Povinec et al., 2017; Tanaka et al., 2014). Precipitation samples collected in Tsukuba, Japan, in 2010 (before the accident) exhibited a tritium level of 2 TU (Matsumoto et al., 2013). However, Matsumoto et al. (2013) take into consideration fluctuations and seasonal variations and thus consider 6 TU as a conservative pre-accident background value for tritium. So far, the highest estimated environmental concentration of tritium after the Fukushima accident were 1342 TU and 433 TU (in rainwater collected 25 km from FDNPP 10 days and 5 weeks after the accident) (Kashiwaya et al., 2017) and 160 TU (in rainwater collected 170 km from FDNPP 10 days after the accident) (Matsumoto et al., 2013), respectively.

In contrast to ^{3}H, contamination levels with more prominent Fukushima-derived fission products such as ^{131}I ($T_{1/2}$ = 8.0 d), ^{134}Cs ($T_{1/2}$ = 2.0 y), and ^{137}Cs ($T_{1/2}$ = 30.0 y) have been well documented in scientific literature. With its much shorter half-life and its nuclear history as a typical reactor nuclide, ^{134}Cs can be regarded as a distinct Fukushima nuclide as it has not been present in the Japanese environment prior to the accident. The activity ratio of $^{134}Cs/^{137}Cs$ (0.98±0.01) (Merz et al., 2013) is a reliable fingerprint for the releases from FDNPP. Strontium-90 ($T_{1/2}$ = 28.8 y) was released in much smaller amounts (about 0.03% of the ^{90}Sr reactor inventories) (Povinec et al., 2013) and is not always easily distinguishable

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from ubiquitous ^{90}Sr fallout stemming mostly from atmospheric nuclear explosions. The laborious separation of the pure beta-emitter ^{90}Sr (in contrast to gamma-emitting ^{131}I and ^{134,137}Cs) explains why monitoring data sets of ^{90}Sr are always shorter than those of the gamma emitting radiocesium nuclides.

Although released in significant amounts, analysis of ^{131}I was hampered by its short half-life. However, long-lived ^{129}I ($T_{1/2}$ = 15.7 My) can be used as a suitable proxy, allowing retrospective assessment of an already decayed ^{131}I contamination (Michel et al., 2005; Pietrzak-Flis et al., 2003), which will also be demonstrated in this study. The ^{129}I/^{131}I atomic ratio measured after the accident was around 16 in precipitation and 32 in soil samples (Miyake et al., 2012; Xu et al., 2013).

Some studies have focused on radionuclide contaminations in surface waters, both on land, e.g., (Konoplev, 2016; Konoplev et al., 2018; Naulier et al., 2017; Suzuki et al., 2018; Wakiyama et al., 2017) and in the Pacific Ocean, e.g., (Casacuberta et al., 2013; Castrillejo et al., 2016; Sanial et al., 2017; Takata et al., 2019; Vives i Batlle et al., 2018). In this study, we add a data set of radionuclides in (primarily fresh) water samples soon after the accident in the vicinity of FDNPP.

2. MATERIALS AND METHODS

Ten water samples were collected in Fukushima Prefecture on April 10, 2011 and passed through a 0.45 µm mesh syringe filter. The particulate fractions on the filters were not further investigated due to very low activity levels. The exact locations and sample types are given in Table S1 and Figure S1 in the Supplementary Data (SD). For this study, we distinguish between three different types of samples: puddle water, paddy water, and seawater. The term puddle water refers to a water sample that has been collected from cracks in the asphalt of a road, whereas paddy water was collected from rice paddy fields. Although the rice paddy

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fields were not fully covered with water at the time of the accident, residual water could be sampled from the edge of the paddy field. The seawater sample #3 was collected from surface of the Pacific Ocean close to the shore. Sampling was done under harsh conditions that resulted from the destroyed infrastructure as a consequence of the March 11, 2011 earthquake and tsunami and from high radiation levels in the restricted areas. Due to this fact, only reachable water samples from surfaces could be collected. This included puddle water, representing an unusual type of surface water.

For the analysis of radiocesium (^{134}Cs, ^{137}Cs), gamma spectrometry was applied as described in the SD. The separation of (radio)strontium was performed with a strontium specific extraction resin (see SD for a detailed description of the separation steps) and determined by liquid scintillation counting (LSC) (Rosenberg et al., 2017). Measurements were performed with a HIDEX^{TM} 300 SL liquid scintillation counter. Tritium was separated from interfering radionuclides by distillation (see SD) and quantified using LSC. Uncertainties were calculated according to DIN ISO 11929 and 32645, respectively (see SD).

An aliquot of each sample material (volumes ranging from 1-38 mL) was used for the analysis of the ^{129}I/^{127}I ratio. Accelerator mass spectrometry (AMS) measurements were performed at ETH Zurich and University of Vienna. Quantification of ^{127}I (for the indirect quantification of ^{129}I via the isotopic ratio) was determined with ICP-MS. A detailed description can be found in the SD.

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3. RESULTS AND DISCUSSION

Tabulated data of the radionuclide analysis are given in Table S2.

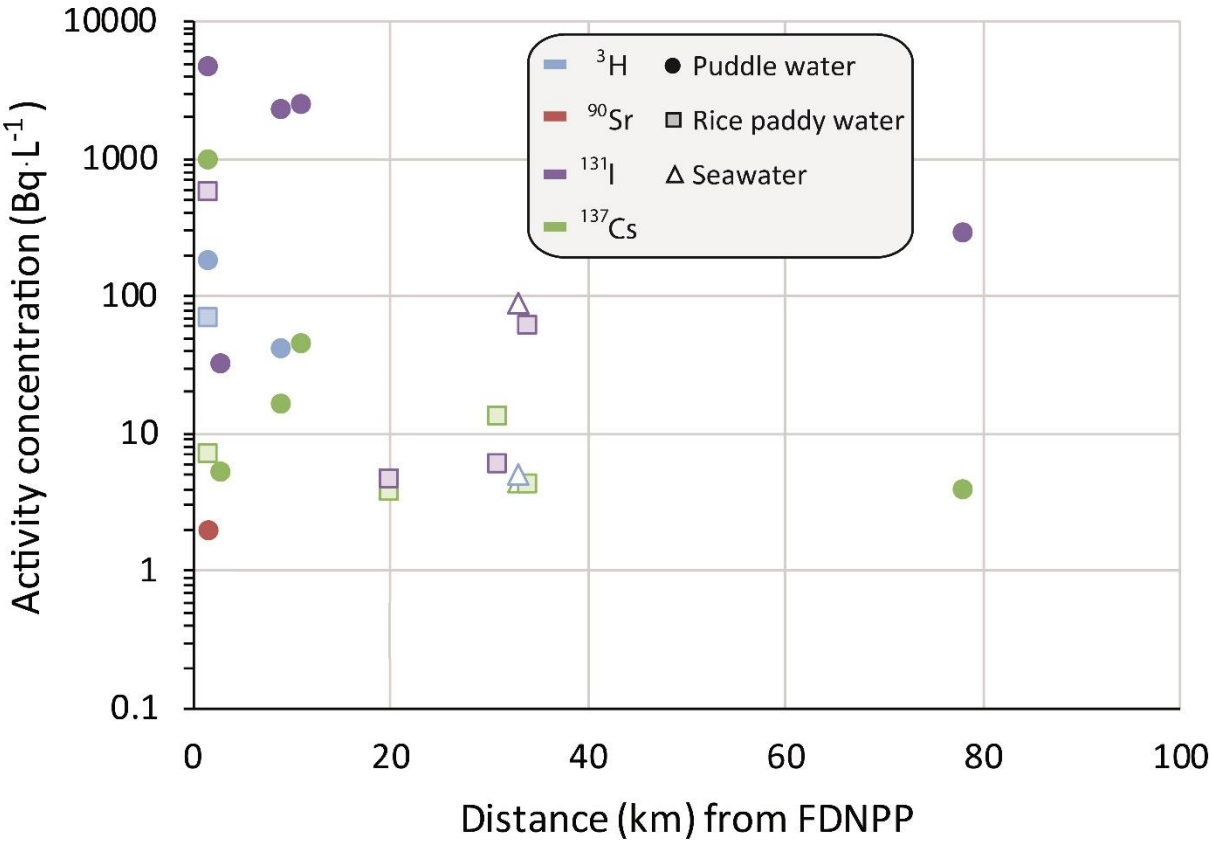

Fig. 1 Activity concentrations [Bq·L^{-1}] decay corrected to April 10, 2011 of ^{3}H, ^{90}Sr, ^{131}I and ^{137}Cs of all samples. ^{131}I was calculated from an ^{129}I/^{131}I atomic ratio of 16 as of March 11, 2011 (Miyake et al., 2012). Due to possible volatilization of ^{129}I during storage, these values represent the minimum activity concentration of ^{131}I.

Four samples exhibited detectable tritium activity concentrations (see Fig. 1). The highest tritium activity concentration was found in a puddle sample (#5Pud), collected approximately 1.5 km from the FDNPP site. The activity in this sample was 1560 ± 17 TU or 184 ± 2 Bq·L^{-1}, which is over 200 times higher than the background activity in Japan (6 TU) (Matsumoto et al., 2013). The paddy water sample (#6Pad) from the vicinity of this puddle, also showed

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relatively high tritium activity concentrations (580 ± 17 TU), illustrating the dilution of contaminated rainwater in the stagnant water in the rice paddy field. A puddle sample (#1Pud) from close to the Fukushima Daini NPP (F2NPP), 11 km south of FDNPP, also exhibited detectable activity concentrations (360 ± 17 TU). Lastly, tritium was also found in significantly elevated levels above background in a seawater sample (#3Sea), about 33 km south of FDNPP (42 ± 17 TU).

The tritium activity concentrations in the puddle water sample #5Pud are remarkably high. For comparison, reactor coolant water from the undamaged FDNNP Unit 5 exhibited tritium activity concentrations of 2260 $Bq \cdot L^{-1}$, only 12 times higher than this environmental water sample (Shozugawa et al., 2016). The tritium level in this puddle water is the highest ever reported in scientific literature after the Fukushima nuclear accident. Kashiwaya et al. (2017) estimated a tritium concentration in precipitation of 1342 TU at a distance of 25 km 10 days after the accident. Our sample #5Pud comes from a much closer location (1.5 km from FDNPP) but was taken 30 days after the accident. Matsumoto et al. (2013) found the highest activity concentration in rainwater from Tsukuba (170 km south of FDNPP), peaking at 160 TU.

Given the washout ratio discussed by Matsumoto et al. (2013) of 1×10^4, this activity concentration in the liquid phase would correspond to an atmospheric concentration of about 18 $Bq \cdot m^{-3}$, which is still 2 orders of magnitude lower than the estimates of atmospheric tritium concentrations in during the earliest stage of the accident (1.5 $kBq \cdot m^{-3}$). Even though these are the highest-ever reported tritium concentrations in surface water, they are still significantly below the WHO regulatory limit of 8.5×10^4 TU for tritium in potable water (World Health Organization (WHO), 2011).

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Puddle water sample #5Pud stands out for its high tritium concentrations. Kakiuchi et al. (2012) found similarly high tritium levels in the free-water tritium (FWT) of plants collected 20 km northwest of FDNPP (167 $Bq \cdot L^{-1}$). Their plant samples were collected at about the same time (4/12-14 and 4/26, 2011) like the water samples in this study (4/10, 2011).

Pacific Ocean water has been analyzed in multiple campaigns for the influx of radionuclides from the crippled FDNPP (Kaizer et al., 2018; Povinec et al., 2013; Povinec et al., 2017). However, many studies analyzed the seawater for its ^{3}H content at a later stage after the accident (and in the course of ship cruises with more samples from non-coastal areas). This explains why our relatively high ^{3}H concentrations (#3Sea) (42 TU) exceed those of (Takahata et al., 2018) (0.8-2.5 TU) that were sampled on 5/7, 2011. The seawater sampled in the course of the KoK cruise in June 2011 (Buesseler et al., 2012; Povinec et al., 2017), also exhibited lower ^{3}H, ^{134}Cs, and ^{137}Cs activity concentrations than our sample. The $^{134}Cs/^{137}Cs$ activity ratio of 1.1±0.3 indicates that virtually the entity of radiocesium in #3Sea is Fukushima-derived, as this is the typical fingerprint of FDNPP emissions. With only one seawater sample included in this study, the results should not be over-interpreted. Nonetheless, we felt that including this single data point in this study would be interesting for the community because of its unusually high degree of contamination.

Strontium-90 was detected in all samples, however, only one sample (#5Pud) exceeded the limit of quantification (LoQ = 1.1 $Bq \cdot L^{-}1$). The small sample volume of #3Sea also exhibited (barely) detectable ^{90}Sr contaminations ($290<x<1100$ $Bq \cdot m^{-3}$), which is close to the higher concentrations found in previous studies, ranging from 0.8 to 85 $Bq \cdot m^{-3}$ for ^{90}Sr and 19-265 $Bq \cdot m^{-3}$ for ^{89}Sr (Casacuberta et al., 2013). Studies that investigated seawater from close proximity to the FDNPP even showed higher contamination levels, i.e. 10^{4} $Bq \cdot m^{-3}$ ^{90}Sr and 10^{5} $Bq \cdot m^{-3}$ ^{137}Cs in seawater in April 2011 (Castrillejo et al., 2016; Japan Atomic Energy Agency, 2018; Japan Nuclear Regulation Authority, 2018). Despite the high uncertainty of

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our value, the impact of the Fukushima nuclear accident is indisputable as the pre-Fukushima background in the northwest Pacific was 1-2 $Bq \cdot m^{-3}$ (Castrillejo et al., 2016).

Activities of long-lived ^{129}I were determined by accelerator mass spectrometry (Bu et al., 2018). Although this radionuclide, due to its long half-life, exhibits low radiotoxicity, it is useful in retrospectively assessing the contamination levels with highly radiotoxic, short-lived ^{131}I, via its distinct $^{129}I/^{131}I$ atomic ratio of 16 (as of March 11, 2011) that is characteristic for the releases from FDNPP (Miyake et al., 2012). Since radioiodine is known to be volatile during storage and processing (Rosenberg and Steinhauser, 2016), the calculated activity concentrations of ^{131}I should be regarded as the minimum concentrations, because some ^{129}I may have escaped during storage. Pre-Fukushima background levels are estimated to be in the range of $2 \cdot 10^{+7}$ atoms ^{129}I per L (Suzuki et al., 2010), which is 2-5 orders of magnitude lower than our samples.

Again, puddle water sample #Pud5 exhibited the highest contamination with radioiodine, peaking in almost 5 $kBq \cdot L^{-1}$ ^{131}I at the time of sampling (2011-04-10), almost one order of magnitude higher than the water from the rice paddy field (#6Pad) in its close proximity. Also, the other puddle water samples (including #2Pud, 78 km south of FDNPP) exhibited high ^{131}I concentrations of ≥ 300 $Bq \cdot L^{-1}$ (see Fig.2). For reference, the Japanese regulatory limits for radionuclides in drinking water were 300 $Bq \cdot L^{-1}$ for isotopes of iodine (notably ^{131}I) and 200 $Bq \cdot L^{-1}$ for isotopes with a half-life > 10 days (notably ^{134}Cs and ^{137}Cs) in the first year after the accident (Merz et al., 2013). The highest ^{129}I concentration in #5Pud (1.4×10^{-3} $Bq \cdot L^{-1}$) exceeds the highest ^{129}I contamination in precipitation in the study by Maruoka et al. (2.5×10^{-4} $Bq \cdot kg^{-1}$) (Maruoka et al., 2017), the calculated ^{131}I activities are in line with the highest ^{131}I activity concentrations reported by (Hazama and Matsushima, 2013) for rainwater (approx. 6 $kBq \cdot L^{-1}$ as of March 20-22, 2011, 200 km from FDNPP).

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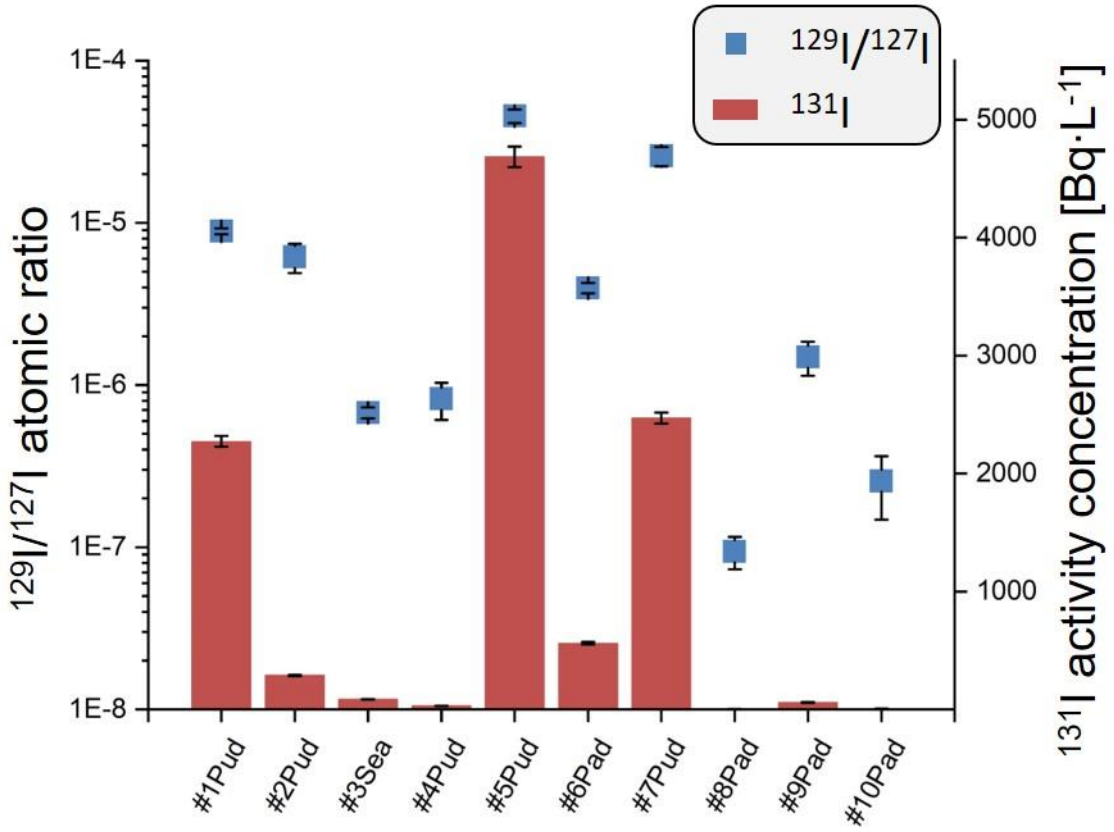

Fig. 2. $^{129}I/^{127}I$ isotopic ratios in the water samples and calculated ^{131}I concentrations at the time of sampling (2011-04-10).

The high contamination of seawater with ^{129}I (2.6×10^{-5} Bq·L^{-1}) should be noted, which is about three orders of magnitude higher than northwest Pacific background levels (Suzuki et al., 2010) of this radionuclide that is ubiquitous in marine ecosystems. Assuming that virtually the entity of ^{129}I originated from Fukushima, an ^{131}I activity concentration of 88 Bq·L^{-1} can be calculated, which is even higher than the previously reported maximum of 77 Bq·L^{-1} at a distance of 30 km from FDNPP (Hou et al., 2013). There is good agreement of our retrospectively determined ^{131}I concentration with the ^{131}I data in seawater presented by Kawamura et al.(Kawamura et al., 2011) Also for the puddle and paddy water samples, pre-Fukushima radioiodine contributes only to a small extent to the present contaminations (^{129}I in

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the range between 1.4×10^{-6} Bq·L^{-1} and 1.4×10^{-3} Bq·L^{-1}). Before the Fukushima accident, the ^{129}I activity concentration in precipitation was around 1.7×10^{-7} Bq·L^{-1} (Xu et al., 2013).

Some radioecological characteristics of these fissions products are nicely illustrated by comparison of puddle water sample #5Pud and rice paddy water sample #6Pad, which are located in close proximity. By applying the principle of isotope dilution analysis (von Hevesy and Paneth, 1913) using tritiated water (from wet deposition) in this location, the tritium ratio $^{3}H_{\#6Pad}/^{3}H_{\#5Pud}$ of 0.37 reflects the dilution of contaminated rainwater with the stagnant water in the rice paddy. For the other radionuclides, any deviation from this ratio may reflect the adsorption on minerals or organic matter, which will affect the rice paddy field, but not (nearly as much) the puddle water that was extracted from cracks in the asphalt of a road. Puddle water does not represent a natural surface water. The radionuclides contained in puddle water are derived from both dry and wet deposition, which, in principle is also true for the adjacent paddy field water (as radionuclides adhere to dust particles and may be deposited on the water surface as "dry" deposition). However, rainwater may also have collected and washed off radionuclides from the street prior to running off into the puddle (with the exception of tritium, which is expected to be present only in liquid form). The effective catchment area of the puddles remain unknown.

The ratio of $^{129}I_{\#6Pad}/^{129}I_{\#5Pud}$ is 0.12, indicating losses of ^{129}I possible through reactions with organic matter. The losses are more pronounced for cationic radiocesium as the ratio of $^{134}Cs_{\#6Pad}/^{134}Cs_{\#5Pud}$ is 0.01 (^{134}Cs is a preferred indicator of the Fukushima nuclear accident as ^{137}Cs may also be present from previous releases). Cesium shows very high affinity to clay minerals (Benedicto et al., 2014; Cornell, 1993; Lee et al., 2017; Nakao et al., 2014), and the low ratio of paddy/puddle water exemplifies the efficient trapping of cesium in the soil of the rice paddy. Only environmental radiostrontium that is known to be (and to remain) highly bioavailable (Merz et al., 2016) and to exhibit little affinity to mineral surfaces, exhibits a

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$^{90}Sr_{\#6Pad}/^{90}Sr_{\#5Pud}$ ratio of 0.4, just like tritium. Due to the fact that the ^{90}Sr activity concentration of sample #6Pad was above the limit of detection but below the limit of quantification, this ratio represents a rather rough estimate and should be interpreted with care. Strontium, an element with medium volatility, was released at the beginning of the accident in disproportionately large amounts compared to other nuclides (likely in the form of radioactive microparticles (Steinhauser, 2018; Zhang et al., 2019), but certainly not via the gas phase (Zhang et al., 2018)). In contrast, cesium, tritium, and iodine, as volatile elements, were released continuously over the several weeks. This may have affected dry deposition sequences in the area. Our results indicate a sorption effect of the various radionuclides in the following order: Cs>I>>Sr~H, which is unusual as one may have expected an order that should rather look something like Cs>I~Sr>>H based on literature (Ciffroy et al., 2009; Smith et al., 2005).

4. CONCLUSIONS

In summary, the Japanese water samples investigated in this study exhibited high levels of contaminations for all studied radionuclides, ^{3}H, ^{90}Sr, ^{129}I (^{131}I), and $^{134+137}Cs$, including the highest-ever reported tritium contamination in an environmental sample affected by the releases from FDNPP. The present study allows for direct comparison of a puddle water sample and a rice paddy water sample that were collected in very close proximity. The ratios between paddy/puddle water vary around 1% for ^{134}Cs and ^{137}Cs, 12% for radioiodine, and around 40% for both ^{3}H and ^{90}Sr. This illustrates the adsorption and retention of radiocesium on natural minerals (in the rice paddy), whereas the concentration differences of ^{3}H and ^{90}Sr between the two waters are mainly dilution driven. This finding emphasizes the high bioavailability of ^{90}Sr released from Fukushima. The concentrations of ^{90}Sr in the water samples of this study were always low (close to the limit of quantification), yet detectable.

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Unfortunately, due to the lack of a forensic indicator (such as short-lived ^{89}Sr), no distinction between Fukushima-derived and global fallout-derived radiostrontium can be made.

ACKNOWLEDGMENTS

We kindly thank the Siebold-Sasse Foundation for financial support for A-EP. Thanks are due to Alex Hölzer, Monika Gorny, and Beate Riebe (all IRS) for their help with iodine sample preparation and data evaluating.

APPENDIX A. SUPPLEMENTARY DATA

The Supplementary Data (SD) is available free of charge online. SD includes a Figure showing the sampling locations (Fig. S1), a tritium spectrum in the LSC (Fig. S2), a graphical illustration of the contamination levels on a map (Fig. S3), a graphical illustration of radionuclide concentrations in #5Pud and #6Pad (Fig. S4), a table with exact sample information (Table S1), a table with the tabulated data of the analysis (Table S2), and a detailed description of the methodology used for radionuclide analysis.

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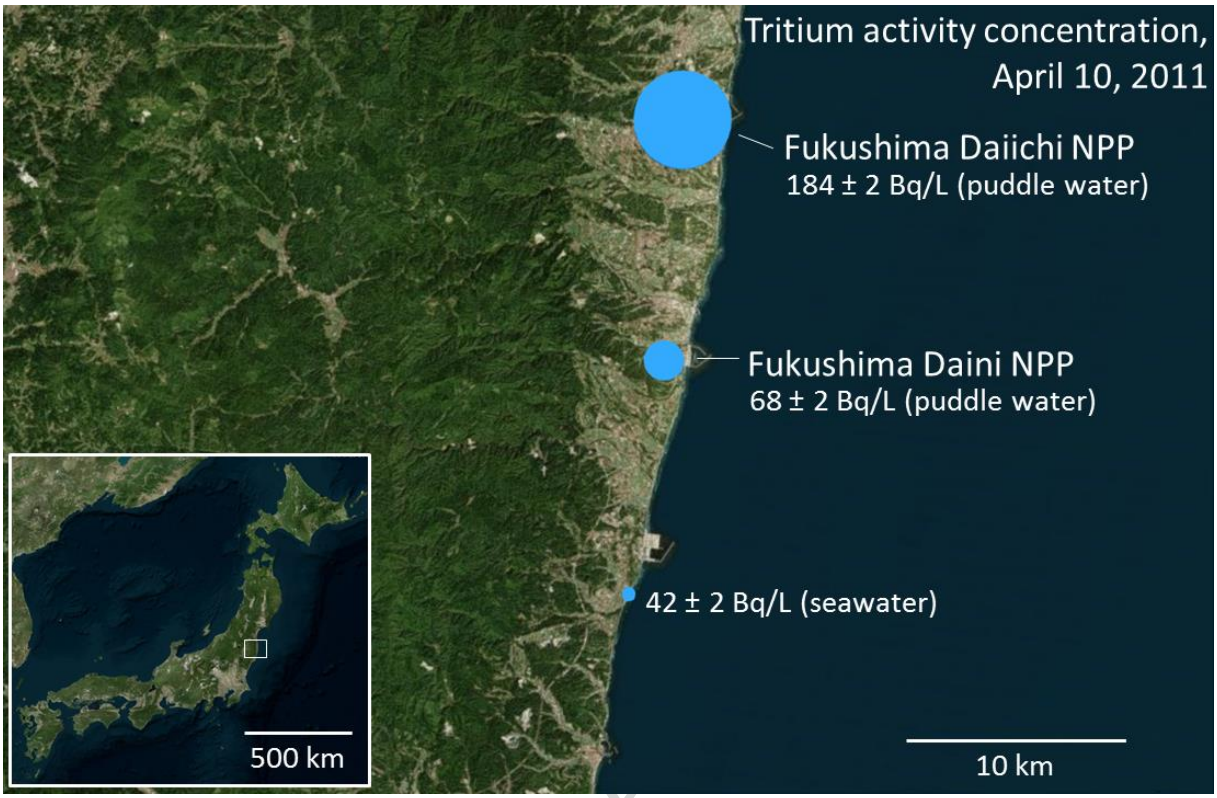
Graphical abstract



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Highlights

- Samples taken 1 mo after the Fukushima accident revealed very high contamination
- Highest tritium concentrations in an environmental sample are reported
- Complete contamination profiles of ^{3}H, ^{90}Sr, ^{129}I, ^{134}Cs, and ^{137}Cs are presented
- Sorption of radionuclides on soil followed an unusual pattern Cs > I >> Sr ~ H

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